

KINETICS OF HYDROCRACKING OF COAL EXTRACT WITH MOLTEN
ZINC CHLORIDE CATALYSTS IN BATCH AND CONTINUOUS SYSTEMSR. T. Struck, W. E. Clark, P. J. Dudd, W. A. Rosenhoover,
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The use of molten zinc chloride as a catalyst for hydrocracking of polynuclear hydrocarbons has been previously described.^(1,2) The superiority of zinc chloride over conventional hydrocracking catalysts was shown for pyrene, coal, and coal extract. Results in batch autoclaves showed that zinc chloride gave more rapid reaction, more complete conversion to gasoline-range naphtha, and a very high octane number without reforming. The high octane number is due primarily to the ability of the Lewis acid, zinc chloride, to maintain acid catalysis in the presence of considerable amounts of nitrogen in the feed, -- thus giving a high percentage of branched-chain hydrocarbons with high octane numbers.

Since the previous reports, a continuous zinc chloride hydrocracker has been built and operated, confirming the batch work, and also providing effluent catalyst for regeneration studies, as well as information on corrosion. A continuous catalyst regeneration unit was also operated, and will be described in the following paper. A complete report on all of the work is available from the U. S. Office of Coal Research.⁽³⁾

The purpose of this paper is to report rate data on the hydrocracking of extract with zinc chloride via a correlation which predicts conversion of extract in both batch and continuous units.

EXPERIMENTALFeedstock

The feedstock used for all of the work described here was a coal extract prepared by continuous extraction of Pittsburgh Seam coal, Ireland Mine, using tetralin solvent at 750°F with a residence time of 40 minutes. Unextracted coal and mineral matter were removed by filtration at 646°F. The final extract represents 81% of the moisture- and ash-free coal (MAF coal). Properties are given in Table I.

A measure of the asphaltic nature of extract is given by solvent fractionation. "Benzene-insolubles" is the fraction of extract insoluble in benzene at its atmospheric boiling point. "Asphaltenes" is the fraction soluble in benzene, but insoluble in cyclohexane, determined by mixing one part of benzene-soluble extract with nine parts of benzene and 100 parts of cyclohexane, by weight, and filtering at room temperature. The fraction soluble in this mixture is termed "oil."

Catalyst

The zinc chloride used was Fisher Scientific Co. certified reagent, 96 to 98% pure, dried before used in a vacuum at 110°C. After this treatment, it contained 1 to 1.5 wt % water and 1 to 1.8 wt % zinc oxide. Before feeding this to the continuous unit, the remaining water was removed by melting the salt under full pump vacuum.

For a number of tests, zinc oxide was added to the zinc chloride to bring the total zinc oxide up to that required for stoichiometric reaction with HCl liberated by sulfur in the extract reacting with zinc chloride (4.65 wt % of the catalyst). The zinc oxide used was Baker and Adamson certified reagent; the lots used were 99.0 to 99.5% pure.

Equipment

The basic unit for the batch hydrocracking tests was a 300-ml rocking autoclave (American Instrument Company, Catalog No. 40-2150). The normal rocking motion of 36 cycles/min about the axis was revised to give 86 cycles/min through an angle of 30° on the end of a 12-inch lever arm. The equipment and procedures have been described previously.⁽¹⁾

The continuous hydrocracking unit flow sheet is given in Figure 1. The reactor is a "stirred-tank" reactor, to which extract, catalyst, and hydrogen are fed separately. Constant inventory in the reactor is maintained by a pressure-drop controller operating on a valve in the "spent" catalyst withdrawal line. The reactor is 3 inches in diameter and contains a liquid inventory of 400 to 600 grams. All products were collected, analyzed, and the results consolidated. Elemental balances were then made and the zinc balance forced by adjusting the residue collected. This avoided errors due to differing bed levels at beginning and end of the balance period. The carbon balance was then forced by adjusting the amount of extract fed (uncertainty existed as to the density in the feed pump). The nitrogen, oxygen, and sulfur balances were forced by assuming the unaccounted-for products to be NH_3 , H_2O , and H_2S , respectively, which have reacted with the catalyst. Chlorine was forced by assuming the unaccounted-for chlorine was present in the catalyst as the double salt $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$. The hydrogen consumption was then obtained by difference between the hydrogen in the products and that in the feedstock (exclusive of H_2 gas). After forcing all elemental balances, the overall material balance also closes, and the conversions reported in Table IV are reported on this basis.

Conversion, as used here, is the conversion of extract to products boiling below 400°C (752°F) at normal atmospheric pressure. It is calculated by subtracting the percentage of +400°C residue from 100%. Because of the heat-sensitivity of the materials involved, the 400°C cut point in a distillation is defined as 240°C in the pot of a simple flask when the pressure is 1 torr.

DISCUSSION OF RESULTS

Results in the continuous unit generally confirmed previous batch results, showing higher conversion at lower levels of zinc oxide. Temperature has the expected result - more rapid reaction at higher temperatures, but at temperatures above 750°F, the maximum liquid yield decreases. Straight run gasolines from zinc chloride hydrocracking show Research Octane Numbers (clear) of 87 to 91 and a high sensitivity to lead. With 3 ml of tetraethyllead per gallon, the RON values rise to 99 to 101. If reformed, the product would be 85 to 90% aromatics, suitable for a high-octane blending stock for gasolines or as a source of benzene via hydrodealkylation.

Kinetic Model

The basic model used to correlate hydrocracking results assumes that extract is composed of many different compounds, each hydrocracking independently at a different rate that can be expressed as a first-order reaction. The situation has been greatly simplified by assuming only three species present: an unconvertible fraction, a fraction which converts rapidly, and a fraction which converts relatively slowly. For simultaneous independent reactions in a batch unit,

$$C_e - C = N_1 C_e e^{-k_1 t} + (1 - N_1) C_e e^{-k_2 t} \quad (1)$$

where " $C_e - C$ " is the convertible material remaining at time " t ", and " N_1 " is the fraction of the convertible material which reacts via the fast reaction. A table of nomenclature is given at the end of the text.

For a single perfectly-mixed, continuous reactor, the probability that a microscopic drop of liquid will have a residence time in the reactor between t and $t + dt$ is $\frac{1}{\tau} e^{-t/\tau} dt$.

where τ = residence time in the continuous unit.

The average fraction of extract unconverted then would be

$$\frac{C_e - C}{C_e} = \frac{1}{\tau} \int_0^{\infty} \left(\frac{C_e - C}{C_e} \right)_B e^{-t/\tau} dt$$

where $\left(\frac{C_e - C}{C_e} \right)_B$ is the fraction unconverted at the time " t " as determined from batch data. Substituting from Equation 1 for $\left(\frac{C_e - C}{C_e} \right)_B$, gives the following:

$$\frac{C_e - C}{C_e} = \frac{1}{\tau} \left[N_1 \int_0^{\infty} e^{-(1+k_1\tau)t/\tau} dt + (1-N_1) \int_0^{\infty} e^{-(1+k_2\tau)t/\tau} dt \right]$$

$$\frac{C_e - C}{C_e} = \frac{N_1}{1 + k_1\tau} + \frac{1 - N_1}{1 + k_2\tau} \quad (2)$$

Evaluation of Constants

The data available consist of 38 runs in the batch autoclave and 14 runs in the continuous unit, covering the following ranges:

	<u>Batch Unit</u>	<u>Continuous Unit</u>
Temperature, °F	700-775	700-800
Partial Pressure of H ₂ , psig	1500-3500	2730-3300
Residence Time, minutes	15-360	22.8-192.6
Catalyst/Extract Weight Ratio	1.0	0.9-1.3
ZnO/ZnCl ₂ Mole Ratio	0.013-0.0765	0.01-0.08
Conversion, Wt % of Extract	41-92	62-89

The more extensive batch data have been used to determine constants in the kinetic equations wherever applicable. However, because of the uncertainty in low residence times inherent in batch runs (i.e., some conversion takes place as the reaction temperature is approached), the continuous unit data have been used to determine the rate constant for the fast reaction.

It is assumed that a certain fraction of the extract fed is not convertible under the conditions of temperature, pressure, and catalyst composition used, even at infinite residence time, although the amount may vary with operating conditions. The extent of possible conversion, C_e , has been determined by plotting conversion versus residence time for each set of conditions (batch data). Tangents drawn to each curve yield the slope, or rate of reaction, dC/dt . These instantaneous rates were then plotted versus conversion yielding results such as shown in Figure 2. The straight lines obtained confirm the fact that the data can be represented as first order reactions and when extrapolated to zero rate of conversion yield C_e . The values of C_e so obtained are listed in Table II as "Observed C_e ". It can be seen that variables of temperature, hydrogen pressure and ZnO/ZnCl₂ ratio all affect the value of C_e obtained. The value of C_e is independent of whether batch or continuous data are involved, since they are equal at infinite residence time.

In order to estimate C_e for conditions other than those at which runs were made, empirical equations have been developed. The first equation applies over the hydrogen partial pressure range of 2500 to 3500 psig:

$$C_e = 90 + \frac{(p - 2500)}{600} + \frac{(750 - T)}{25} + 10(0.08 - x) \quad (3)$$

where p = partial pressure of hydrogen, psig.
 T = temperature, °F.
 x = mole ratio of $ZnO/ZnCl_2$.

For the pressure range, $p = 1500$ to 2500 :

$$C_e = 90 - \frac{(2500 - p)}{200} + \frac{(750 - T)}{25} + 10(0.08 - x) \quad (4)$$

The calculated values of C_e for the batch runs are also listed in Table II, and compare well with the observed values. Equations 3 and 4 were used in calculating conversions for both batch and continuous runs. The equations illustrate the facts that C_e increases at low levels of ZnO , at higher pressures, and at lower temperatures (within the 700 to 800°F range).

At long residence times where the fast reaction is substantially complete, and when N_1 is constant, Equation 1 shows that a plot of $\log(C_e - C)$ versus residence time should be a straight line:

$$\log(C_e - C) = \log(1 - N_1) C_e - k_2 t.$$

The slope of such a line is k_2 and the intercept on the ordinate is $\log[(1 - N_1)C_e]$. This provides a technique for determining k_2 and N_1 . Figure 3 is a representative plot of this type. Again, we see the confirmation of straight lines if we ignore runs at low residence times where the fast reaction is incomplete.

The values of k_2 and N_1 from plots like Figure 3 are listed in Table II. It can be seen that 67 to 81% of the convertible extract reacts via the fast reaction (N_1). To simplify further calculations, a constant value of $N_1 = 0.75$ has been taken as representative of all conditions.

The reaction rate constants for the slow reaction, k_2 , have been plotted for the hydrogen pressure level of 2500 psig as an Arrhenius plot in Figure 4. Because the ratio of ZnO to $ZnCl_2$ is an important parameter, only two points are available at a single condition. A line was drawn through these points and lines at other $ZnO/ZnCl_2$ ratios drawn parallel to it. A line at $ZnO/ZnCl_2 = 0.02$ was interpolated for future use with continuous unit data. Based on the relatively mild effect of pressure on k_2 shown in Table II, the values in Figure 4 have been used for estimating conversions at all pressures.

The remaining constant in Equations 1 and 2 is k_1 , the reaction rate constant for the fast reaction. This has been determined from the continuous unit data by using the data from one run at each condition and solving for k_1 in Equation 2. Values of C_e were calculated from Equations 3 or 4, those for k_2 were taken from Figure 4, and N_1 was taken as 0.75. Generally, the run with the lowest conversion in each set was used to calculate k_1 , since it would be most representative of the fast reaction.

The values of k_1 obtained are listed in Table IV along with other information on the continuous runs. An Arrhenius plot of k_1 is given in Figure 5, showing the desired straight line and indicating an activation energy for the fast reaction of 35 kcal/g mole. It will be noted that the values of k_1 are independent of the $ZnO/ZnCl_2$ ratio, in contrast to those for k_2 . Since the range of hydrogen pressures was quite narrow in the continuous data, the effect of hydrogen pressure, if any, on k_1 could not be determined.

The energy of activation of 35 kcal/g mole indicates that the rate-determining step involves a chemical reaction rather than being limited by accessibility of hydrogen in the bulk liquid or through a boundary film. It coincides with the value found by Weller⁽⁴⁾ for hydrogenation of asphaltenes from coal with tin catalyst. This also was a first-order reaction.

Comparison of Calculated and Observed Conversions

The values of C_e , N_1 , k_1 and k_2 as determined above were used in Equation 1 to predict the conversion for each run in the batch unit. Table III compares these calculated conversions with those actually observed. The "fit" is quite good, particularly at high conversion levels. The poorest fit occurs at low conversions and low hydrogen pressures. This suggests that the reaction rate constant for the fast reaction, k_1 , actually is a function of pressure, although the data do not permit this relationship to be properly defined.

Similar calculations for data from the continuous unit via Equation 2 are shown in Table IV. Again, the observed and predicted conversions show good agreement. The experimental data and calculated curves for 3000 psia of hydrogen are shown in Figure 6. The "fit" is quite good except for a few of the 775°F points at 0.07 to 0.08 mole ratio $ZnO/ZnCl_2$, which show 2 to 6% higher conversions than predicted

CONCLUSIONS

The kinetic model which assumes that the hydrocracking of coal extract with zinc chloride catalyst can be represented by two or more simultaneous first-order reactions has been shown to represent both batch and continuous unit data. An average of 75% of the extract converts via a fast reaction with an activation energy of 35 kcal/g mole. The reaction rate constant for this reaction is affected somewhat by hydrogen pressure, but is independent of the ratio of ZnO to $ZnCl_2$. The rate constant for the slow reaction, which may be lower by a factor up to 40 times, is independent of hydrogen pressure (1500-3500 psig), but a strong function of how much ZnO is present.

ACKNOWLEDGEMENT

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NOMENCLATURE

- C = conversion of extract to -400°C products, wt % of MAF extract.
- C_e = conversion at which the rate of conversion becomes zero.
- k_1 = reaction rate constant for extract conversion via the fast reaction, min.^{-1}
- k_2 = reaction rate constant for extract conversion via the slow reaction, min.^{-1}
- N_1 = fraction of C_e which occurs via the fast reaction.
- p = partial pressure of hydrogen, psig.
- T = temperature.
- t = residence time in a batch or plug flow reactor, min.
- x = $ZnO/ZnCl_2$ mole ratio in the catalyst.
- τ = Average residence time in the continuous reactor, = weight of liquid phase in the reactor divided by the weight rate of liquid product/min. The liquid is the "natural" liquid existing at reactor conditions, i.e., catalyst plus unvaporized oil.

References

- (1) Zielke, C. W., Struck, R. T., Evans, J. M., Costanza, C. P., and Gorin, Everett, I&EC Process Design & Dev., 5, April 1966, p 151-157.
- (2) Zielke, C. W., Struck, R. T., Evans, J. M., Costanza, C. P., and Gorin, Everett, I&EC Process Design & Dev., 5, April 1966, p 158-164.
- (3) Summary Report I - Consol Synthetic Fuel Development, U. S. Office of Coal Research, Contract 14-01-0001-310, 1968.
- (4) Weller, Sol, Pelipetz, M. G., and Friedman, Sam, Ind. Eng. Chem., 43, p 1572 (1951).

TABLE I
Properties of Coal and Extract Used

	Ireland <u>Mine Coal</u>	Coal <u>Extract</u>
	MF Basis	
Volatile Matter	40.32	
Fixed Carbon	46.66	
FeS	0.08	
FeS ₂	4.19	
Other Ash	10.15	
	MAF Basis	
Hydrogen	5.73	6.03
Carbon	81.90	84.65
Nitrogen	1.58	1.53
Oxygen (by diff.)	8.61	6.14
Sulfur	2.18	1.65
<u>Solvent Fractions</u>		
Benzene-insolubles		33
Asphaltenes		47
Oil		20

TABLE II
Values of C_e, N₁ and k₂ Determined from Batch Runs

Temp., °F	ZnO/ZnCl ₂ Mole Ratio	H ₂ Partial Pressure, psig	C _e , Wt % of Extract		N ₁ (3)	k ₂ (4) min. ⁻¹
			Observed (1)	Calculated (2)		
700	0.013	1500	87	87.7	0.670	0.0058
700	0.013	2500	92	92.7	0.712	0.0048
750	0.03	2500	91	90.5	0.736	0.020
750	0.03	3500	92	92.1	0.740	0.030
750	0.0765	1500	85	85.0	0.750	0.0062
750	0.0765	2500	90	90.0	0.773	0.0063
775	0.0765	2500	88	89.0	0.810	0.021
775	0.0765	3500	(90)	89.6	0.788	--

- (1) Intercepts on Figure 2 and similar plots.
- (2) Calculated from Equations 3 and 4.
- (3) Determined from intercepts on Figure 3 and similar plots.
- (4) From the slopes of Figure 3 and similar plots.

TABLE III
Calculated and Observed Conversions for Batch Runs

Temp., °F	ZnO/ZnCl ₂ Mole Ratio	H ₂ Partial Pressure, psig	k ₁ ⁽¹⁾ min. ⁻¹	Residence Time, ⁽²⁾ min	Conversion Wt % of Extract	
					Observed	Calculated ⁽³⁾
700	0.013	1500	0.078	15	41.2	46.8
				60	61.2	71.0
				120	71.0	76.1
				180	76.6	79.3
				360	82.6	84.3
750	0.03	2500	0.24	15	49.1	49.5
				60	70.6	73.6
				120	78.8	80.5
				180	83.4	83.9
				360	89.0	89.2
750	0.03	3500	0.24	15	78.6	73.1
				60	87.1	85.1
				120	91.6	89.9
				180	92.1	91.4
750	0.0765	1500	0.24	15	52.0	64.0
				60	68.8	70.5
				120	74.9	74.9
				180	80.0	78.1
				360	83.4	82.8
775	0.0765	2500	0.43	15	58.1	67.8
				60	76.7	74.6
				120	80.5	79.3
				180	83.8	82.7
				360	88.3	87.7
775	0.0765	3500	0.43	15	71.3	71.9
				60	81.9	80.2
				120	86.4	86.2
				180	87.6	87.5
				360	87.7	88.0
775	0.0765	3500	0.43	15	71.7	73.5
				60	80.4	82.6
				120	83.5	87.2
				180	86.5	89.5
				360	89.9	90.0

(1) From Figure 5.

(2) Residence time at reaction temperature.

(3) Calculated from Equation 1.

TABLE IV

Calculation of Rate Constants and Comparison of
Experimental and Calculated Conversions in Continuous Unit

Temp., °F	ZnO/ZnCl ₂ Mole Ratio	H ₂ Pressure psig	Residence Time, min	C _e ⁽¹⁾	k ₂ ⁽²⁾ min. ⁻¹	k ₁ ⁽³⁾ min. ⁻¹	Conversion Wt % of Extract	
							Observed	Calculated
775	0.07	3040	46.7	89.5	0.021	0.43	75.0 ⁽⁴⁾	75.0
↓	0.07	3000	95.0	↓	↓	↓	83.1	80.5
↓	0.09	2860	96.8	↓	↓	↓	82.0	80.5
↓	0.08	2860	101.0	↓	↓	↓	85.0	80.7
↓	0.08	3100	102.6	90.0	↓	↓	87.1	81.4
750	0.08	3300	22.8	91.0	0.0063	0.24	61.7	60.7
↓	↓	3090	51.2	↓	↓	↓	68.8 ⁽⁴⁾	68.6
↓	↓	3040	105.0	↓	↓	↓	74.1	74.6
750	0.02	3190	24.3	92.0	0.051	0.24	71.7 ⁽⁴⁾	71.7
↓	↓	3150	26.6	↓	↓	↓	72.2	72.0
↓	↓	3040	102.0	↓	↓	↓	84.0	87.9
800	0.08	2815	102.0	88.5	0.070	0.72	86.6	85.0
776	0.02	2730	111.7	90.0	0.16	0.43	88.5	87.5
700	0.02	3210	80.5	93.0	0.003	0.078	64.3 ⁽⁴⁾	64.3

(1) Calculated via Equation 3.

(2) From Figure 4.

(3) Calculated via Equation 2 using $N_1 = 0.75$.

(4) Experimental point used to calculate k_1 .

SIMPLIFIED FLOW DIAGRAM OF

CONTINUOUS HYDROCRACKER USING ZINC CHLORIDE CATALYST

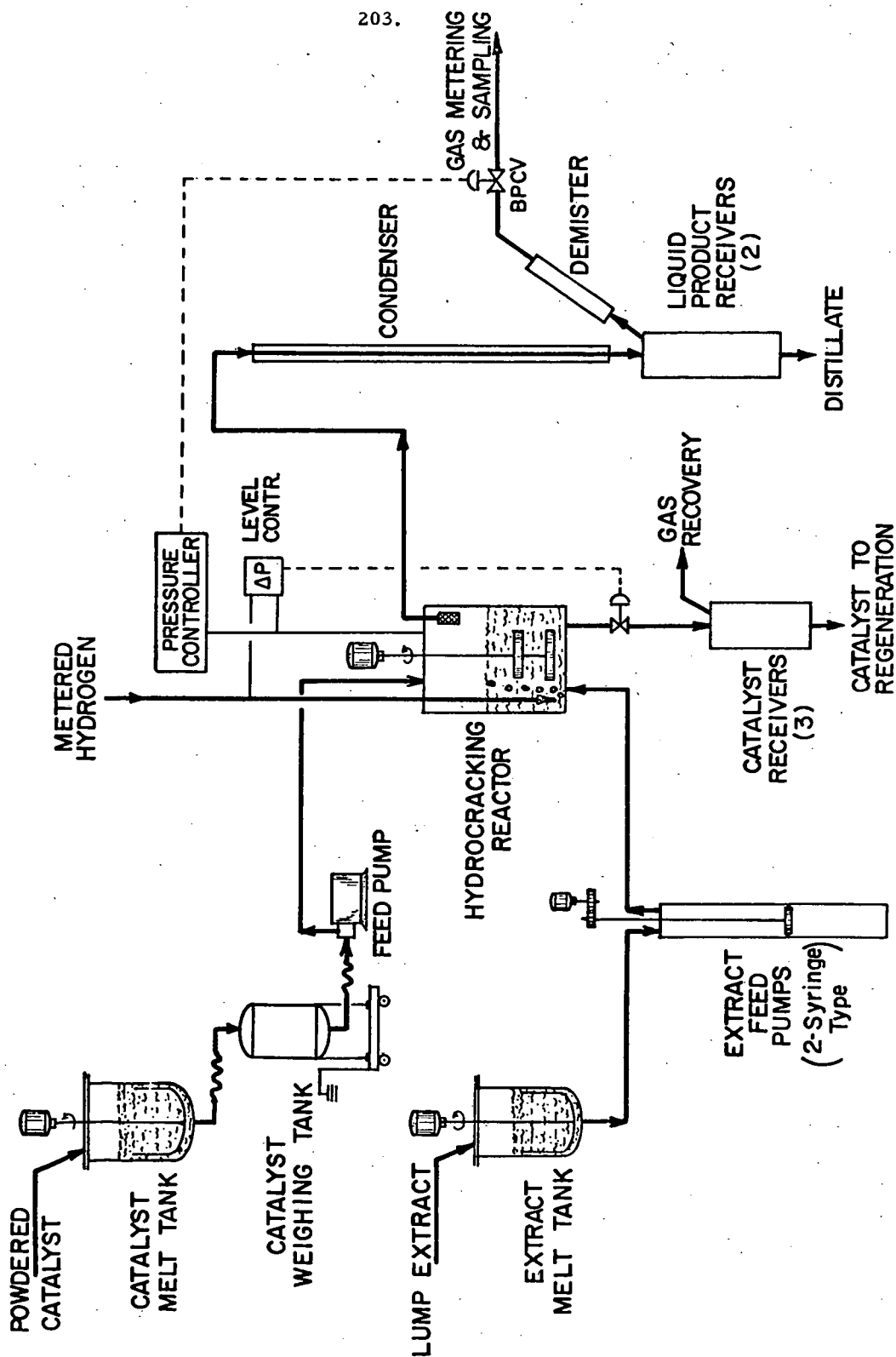


Figure 2

EXTRAPOLATION OF BATCH RATE
DATA TO DETERMINE C_e

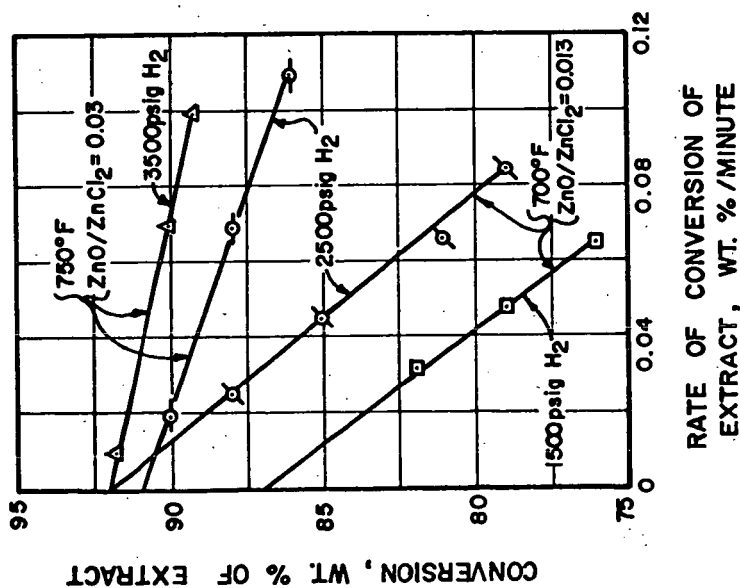


Figure 3

RESIDUE REMAINING VS RESIDENCE TIME

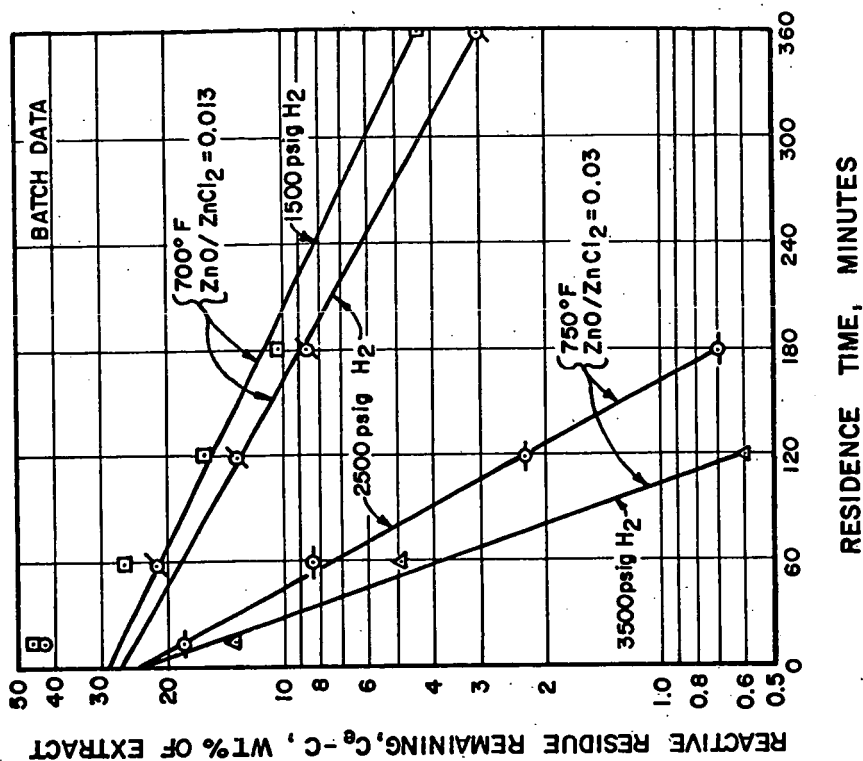


Figure 4

REACTION RATE CONSTANT FOR THE SLOW
REACTION vs RECIPROCAL TEMPERATURE

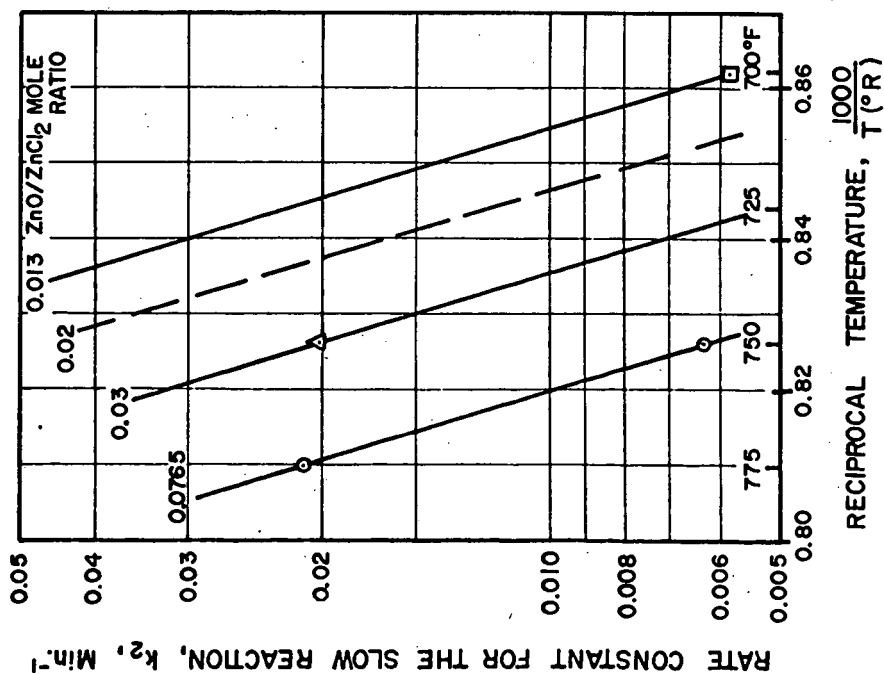


Figure 5

REACTION RATE CONSTANT FOR THE FAST
REACTION vs RECIPROCAL TEMPERATURE

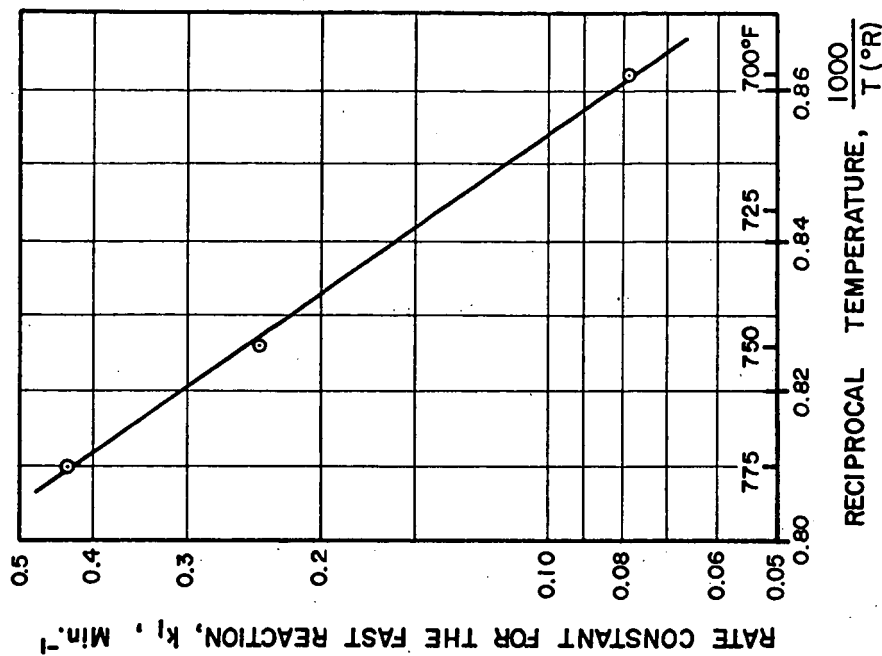


Figure 6

VARIATION OF CONVERSION WITH RESIDENCE TIME IN THE CONTINUOUS REACTOR

